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(21) International Application Number: PCT/US99/02926 (22) International Filing Date: 10 February 1999 (10.02.99) (30) Priority Data: 09/047,551 25 March 1998 (25.03.98) US (71) Applicant: BETZDEARBORN INC. [US/US]; 4636 Somerton Road, P.O. Box 3002, Trevose, PA 19053-6783 (US). (72) Inventor: ARHANCET, Graciela, B.; 20667 Castle Ben Drive, Katy, TX 77450 (US). (74) Agents: VON NEIDA, Philip, H. et al.; BetzDearborn Inc., 4636 Somerton Road, Trevose, PA 19053-6783 (US).		(81) Designated States: BR, CA, CN, JP, KR, PL, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: COMPOSITIONS AND METHODS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION (57) Abstract Synergistic composition and method of use are disclosed. The compositions comprise a quinone methide derivative and a hydroxylamine compound. These compositions demonstrate synergism at inhibiting the polymerization of a vinyl aromatic monomer. Preferably the quinone methide derivative is 2,6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone and the hydroxylamine compound is N,N-bis(hydroxypropyl)-hydroxylamine.		

COMPOSITIONS AND METHODS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION

5 FIELD OF THE INVENTION

The present invention pertains to compositions for use in inhibiting vinyl aromatic monomer polymerization.

10 BACKGROUND OF THE INVENTION

Common industrial methods for producing styrene typically include separation and purification processes such as distillation to remove unwanted impurities. Unfortunately, purification processes carried out at
15 elevated temperatures result in an increased rate of undesired polymerization. Distillation is generally carried out under vacuum to minimize loss of monomer. The presence of oxygen, which is typically excluded from styrene distillation, will also promote polymerization of the monomer.

20

This polymerization results not only in loss of desired monomer end-product, but also in the uses of production efficiency caused by polymer formation and/or agglomeration of polymer on process

equipment. Thermal polymerization, which typically occurs during distillation, of styrene monomer results in the formation of normal (i.e., linear) polymer. This resulting polystyrene polymer is characterized by its glassy and transparent appearance and its solubility in the styrene monomer and many organic solvents.

The compounds generally used commercially to inhibit polymerization of vinyl aromatic monomers are of the dinitrophenol family. For example, U.S. Pat. No. 4,105,506, Watson et al. teaches the use of 2,6-dinitro-p-cresol as a polymerization inhibitor for vinyl aromatic compounds. U.S. Pat. No. 4,466,905, Butler et al. teaches that a combination of 2,6-di-nitro-p-cresol and p-phenylenediamine will inhibit polymerization in a distillation column when oxygen is present. U.S. Pat. No. 4,774,374, Abruscato et al. teaches compositions for inhibiting the polymerization of vinyl aromatic compounds. The composition is an oxygenated product of the reaction of N-aryl-N'-alkyl-p-phenylenediamine with oxygen. U.S. Pat. Nos. 5,426,257 and 5,489,718, Arhancet, teach methods and compositions for inhibiting the polymerization of vinyl aromatic monomers comprising an oxime compound and a hydroxylamine compound and/or a phenylenediamine.

The use of hydroxylamine compounds for preventing polymerization of vinyl aromatic compounds is disclosed in U.S. Patent 2,965,685, Campbell. Their use in combination with phenylenediamines is disclosed in U.S. Pat. Nos. 5,396,004 and 5,510,547, Arhancet et al.

U.S. Pat. Nos. 4,003,800 and 4,040,911, Bacha et al., teach methods for inhibiting the polymerization of styrene utilizing a quinone alkide compound without or with a hindered phenol compound,

respectively. Preferably, the quinone alkide is a methide such as 2,6-di-
butyl-4-methenyl quinone methide.

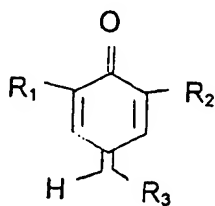
U.S. Pat. No. 5,616,774, Evans et al., discloses processes and
5 compositions for inhibiting the polymerization of vinyl aromatic monomers
using a 7-aryl quinone methide. U.S. Pat. No. 5,583,247, Nesvadba et
al., teaches inhibiting the polymerization of ethylenically unsaturated
monomers with a 7-substituted quinone methide.

10 None of these references has taught or suggested employing a
hydroxylamine compound and a quinone methide derivative together to
inhibit the polymerization of a vinyl aromatic monomer.

DETAILED DESCRIPTION OF THE INVENTION

15 Compositions comprising a quinone methide derivative and a
hydroxylamine are provided. These compositions have utility in vinyl
aromatic monomers for inhibiting the unwanted polymerization therein.

20 The quinone methide derivatives generally have the formula:



wherein:

R₁ and R₂ are independently H, C₄ to C₁₈ alkyl; C₅ to C₁₂ cycloalkyl;
30 or C₇ to C₁₅ phenylalkyl, and

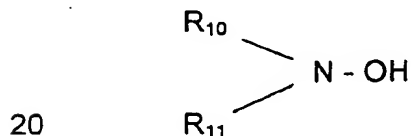
Preferably, R_1 and R_2 are tert-butyl, tert-amyl, tert-octyl, cyclohexyl, α -methylbenzyl or α,α -dimethylbenzyl; with tert-butyl, tert-amyl or tert-octyl most preferred.

- 5 R_3 is preferably aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, hydroxy, nitro, amino, carboxy, or mixtures thereof.

Means for preparing these compounds may be found in U.S. Pat. No. 4,032,547, the contents of which are wholly incorporated by
10 reference to herein.

Preferably, the quinone methide derivative is 2, 6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone.

- 15 The hydroxylamine compounds useful in the present invention generally have the formula



- wherein R_{10} and R_{11} are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have about three to about twenty carbon atoms. The preferred hydroxylamine
25 compound is N, N-bis(hydroxypropyl) hydroxylamine.

The compositions of the present invention are effective at inhibiting polymerization of vinyl aromatic monomers under processing conditions. These processing conditions include but are not limited to preparation,
30 purification, distillation and vacuum distillation processes.

Styrene, for example, is typically processed at temperatures between 95° and 125°C. The compositions of the present invention are effective at inhibiting the polymerization of styrene over this range of temperatures.

5

The vinyl aromatic monomers that are treated by the compositions of the present invention include but are not limited to styrene, bromostyrene, divinylbenzene, and α -methylstyrene. The compositions of the present invention are particularly efficacious at inhibiting the polymerization of styrene monomer.

10

The total amount of quinone methide derivative and hydroxylamine compound used in the methods of the present invention is that amount which is sufficient to inhibit polymerization of vinyl aromatic monomers.

15

This amount will vary according to the conditions under which the vinyl aromatic monomer is being processed, contaminants in the system and the temperature of the system. At higher processing temperatures and higher monomer contamination, larger amounts of the inhibiting composition are required.

20

For purposes of the present invention, the term "effective inhibiting amount" is that amount which is effective at inhibiting vinyl aromatic monomer polymerization. Preferably, this amount ranges from about 1 part to about 10,000 parts of quinone methide derivative and hydroxylamine compound per 1 million parts of monomer. Most preferably, this amount will range from about 1 part total to about 1000 parts per million parts monomer.

25

Accordingly, it is possible to produce a more effective vinyl aromatic monomer polymerization inhibiting treatment than is obtained by the use of either compound by itself when measured at comparable treatment levels. This synergism or enhanced activity between
5 components allows for the concentration of each of the components to be lowered and the total quantity of polymerization inhibitor required, particularly at higher temperatures, may be lowered while achieving a commensurate level of polymerization inhibition.

10 As such, the weight ratio of quinone methide derivative to hydroxylamine compound will generally range from about 9:1 to about 1:9 with a weight ratio of about 2:3 to about 1:1 preferred. Most preferred is a weight ratio of about 1:1.

15 The compositions of the present invention can be introduced into the vinyl aromatic monomer by any conventional method at any point of the processing system, either as separate and individual ingredients or as a combination of ingredients.

20 The compositions of the present invention may be added to the vinyl aromatic monomer as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with the individual ingredients of the composition and the vinyl aromatic monomer to be treated may be employed. It is often desirable to dissolve the
25 inhibitors in the monomer to which the inhibitor is being added to avoid introducing additional impurities in the monomer.

In order to more clearly illustrate the invention, the data set forth below were developed. The following examples are included as being illustrations of the invention and should not be construed as limiting the scope thereof.

5

Examples

Uninhibited styrene (5 mL) was placed in a test tube and the appropriate amount of treatment was added. The tube was capped with a
10 rubber septum and argon was bubbled through the liquid at 10 mL/min. for 3 minutes. The tubes were then placed in an oil bath heated to 110°C for 2 hours. The amount of polystyrene formed was determined by methanol precipitation. The results of this testing are presented in Table I.

15

TABLE I

Uninhibited Styrene Test
110°C

20

<u>Treatment</u>	<u>Dose (ppm)</u>	<u>% Polymer</u>
Blank	-	6.07
A	400	0.46
B	400	1.36
25 A/B	200/200	0.03

Treatment A is 2, 6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone

Treatment B is N,N-bis(hydroxypropyl)hydroxylamine (HPHA)

The results presented in Table I demonstrate that the inventive composition is more effective than either ingredient by itself. Synergism is demonstrated at a 1 to 1 weight/weight ratio.

5 Further testing was performed using a known inhibitor compound, dinitro ortho cresol (DNOC) as a comparative inhibitor. 100 mL of uninhibited styrene was placed in a 250 mL three-necked flask fitted with a bubbler, a septa, and a condenser. The appropriate treatment was added and argon was bubbled through the solution at 10 mL/min. for 10
10 minutes. While argon sparging continued, the flask was immersed in an oil bath heated to 120°C. 5.0 mL samples were taken every 30 minutes and the amount of polymer formed was determined by methanol precipitation. Results of this testing are presented in Table II.

15

TABLE II

Uninhibited Styrene Test
120°C

20	Time (Min.)	Percent Polymer			
		Run 1	Run 2	Run 3	Run 4
	0	0	0	0	0
	30	0.02	0.09	0.03	0.03
	60	0.10	0.22	0.12	0.11
25	90	0.27	0.49	0.22	0.23
	120	0.50	0.96	0.30	0.33
	150	0.72	1.47	0.45	0.43
	180	0.95	2.10	0.59	0.53
	210	1.17	3.13	0.75	0.64
30	240	1.39	4.31	1.00	0.72
	270	1.66	5.79	1.30	0.81
	300	2.16	-----	1.56	0.88

Run 1 is DNOC

Run 2 is 2, 6-di-tert-butyl-4-benzylidene-cyclo-2, 5-dienone

Run 3 is 300 ppm of 2, 6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone
and 300 ppm of HPHA

- 5 Run 4 is 200 ppm of 2,6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone
and 300 ppm of HPHA

This testing demonstrates that the inventive composition at 1:1
and 2:3 ratios was more effective than the quinone methide derivative
10 and DNOC by themselves.

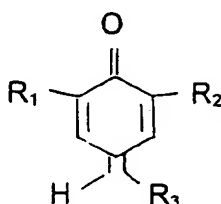
While this invention has been described with respect to particular
embodiments thereof, it is apparent that numerous other forms and
modifications of this invention will be obvious to those skilled in the art.

- 15 The appended claims and this invention generally should be construed to
cover all such obvious forms and modifications which are within the true
spirit and scope of the present invention.

Having thus described the invention, what I claim is:

1. A method for inhibiting the polymerization of vinyl aromatic monomers comprising adding to said monomers an effective polymerization inhibiting amount of a composition comprising (A) a
 5 quinone methide derivative having the formula

10



wherein:

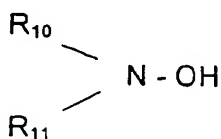
- 15 R_1 and R_2 are independently C_4 to C_{18} alkyl; C_5 to C_{12} cycloalkyl; or C_7 to C_{15} phenylalkyl, and

R_3 is aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, hydroxy, nitro, amino, carboxy, or mixtures thereof; and

20

- (B) a hydroxylamine compound having the formula

25



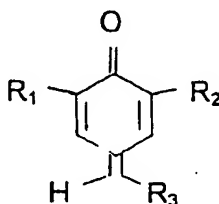
wherein R_{10} and R_{11} are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have about three to about twenty carbon atoms.

2. The method as claimed in claim 1 wherein said quinone methide derivative is 2,6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone.
3. The method as claimed in claim 1 wherein said hydroxylamine compound is a hydroxyalkylhydroxylamine.
4. The method as claimed in claim 3 wherein said hydroxylamine compound is N,N-bis(hydroxypropyl)hydroxylamine.
5. The method as claimed in claim 1 wherein said vinyl aromatic monomer is selected from the group consisting of styrene, bromostyrene, divinylbenzene and α -methylstyrene.
6. The method as claimed in claim 1 wherein said vinyl aromatic monomer has a temperature of about 95° to 125°C.
7. The method as claimed in claim 1 wherein said composition is added to said monomer in an amount ranging from about 1 to about 10,000 parts per million parts of said monomer.
8. The method as claimed in claim 1 wherein the weight ratio of (A) to (B) is about 9:1 to about 1:9.
9. The method as claimed in claim 1 wherein the weight ratio of (A) to (B) is about 9:1 to about 2:3 to about 1:1.
10. The method as claimed in claim 1 wherein the weight ratio of (A) to (B) is about 1:1.

11. The method as claimed in claim 1 wherein (A) is 2, 6-di-tert-butyl-4-benzylidene-cyclo-2, 5-dienone and (B) is N,N-bis(hydroxypropyl)hydroxylamine.

12. A composition comprising (A) a quinone methide derivative having the formula:

5



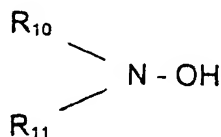
10 wherein:

R₁ and R₂ are independently C₄ to C₁₈ alkyl; C₅ to C₁₂ cycloalkyl; or C₇ to C₁₅ phenylalkyl, and

R₃ is aryl, or aryl substituted with C₁ to C₆ alkyl, alkoxy, hydroxy, nitro, amino, carboxy, or mixtures thereof, and

(B) a hydroxylamine compound having the formula

20



wherein R₁₀ and R₁₁ are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have about three to about twenty carbon atoms.

13. The composition as claimed in claim 12 wherein said quinone methide derivative is 2,6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone.
14. The composition as claimed in claim 12 wherein said hydroxylamine compound is a hydroxyalkyl hydroxylamine.
15. The composition as claimed in claim 14 wherein said hydroxylamine compound is N,N-bis(hydroxypropyl)hydroxylamine.
16. The composition as claimed in claim 12 wherein the weight ratio of (A) to (B) is about 9:1 to about 1:9.
17. The composition as claimed in claim 12 wherein the weight ratio of (A) to (B) is about 2:3 to about 1:1.
18. The composition as claimed in claim 12 wherein the weight ratio of (A) to (B) is about 1:1.
19. The composition as claimed in claim 12 wherein (A) is 2,6-di-tert-butyl-4-benzylidene-cyclo-2,5-dienone and (B) is N,N-bis(hydroxypropyl) hydroxylamine.
20. The composition as claimed in claim 19 wherein the weight ratio of (A) to (B) is about 2:3 to about 1:1.
21. The composition as claimed in claim 12 which has utility as a vinyl aromatic monomer polymerization inhibitor.

22. The composition as claimed in claim 12 wherein there is synergism between (A) and (B) as a vinyl aromatic monomer polymerization inhibitor.
23. The composition as claimed in claim 12 further comprising styrene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/02926

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C09K 13/00; C07C 7/20

US CL : 252/397; 585/3.4

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/397; 585/3.4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT ABSTRACTS, APS TEXT SEARCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,426,257 A (ARHANCET) 20 June 1995, col. 2, lines 13-39.	1-23
Y	US 4,040,911 A (BACHA et al) 09 August 1977, col. 1, lines 60-68; col. 2, lines 1-36.	1-23
Y	US 5,396,004 A (ARHANCET et al) 07 March 1995, col. 1, lines 51-60.	1-23
Y	US 5,616,774 A (EVANS et al) 01 April 1997, col. 2, lines 61-67; col. 3, lines 1-33.	1-23
Y	US 5,583,247 A (NESVADBA et al) 10 December 1996, col. 2, lines 25-67; col. 3, lines 1-61.	1-23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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30 MAR 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/02926

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,510,547 A (ARHANCET et al) 23 April 1996, col. 1, lines 50-59.	1-23
Y	US 4,003,800 A (BACHA et al) 18, January 1977, col. 1, lines 60-67; col. 2, lines 1-27.	1-23
Y	US 5,489,720 A (ARHANCET) 06 February 1996, col. 1, lines 39-50.	1-23
A	US 5,540,861 A (GROSSI et al) 30 July 1996.	1-23
A	US 5,562,863 A (ARHANCET) 08 October 1996.	1-23
A	US 4,237,326 A (FUGA et al) 02 December 1980.	1-23

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